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Polysilanes belong to a new class of polymers with strong electron delocalization in the main chain. Electronic properties are strongly related to conformation and regularity of the macromolecular structure. Some new synthetic methods which increase structural control in polysilanes will be presented: ring-opening polymerization, and polymer modications.. Block and graft copolymers based on polysilanes will be discussed.

Polyphosphazenes with narrow molecular weight distribution and with functional groups are prepared by the catalyzed polymerization of phosphoranimines. Mechanistic aspects of this reaction will be covered.

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TOWARDS WELL-DEFINED POLYSILYLENES AND POLYPHOSPHAZENES

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INTRODUCTION

Polymer synthesis made a tremendous progress in recent years and was transformed to a real macromolecular engineering technique. It is possible to prepare polymers with controlled molecular weight, with low polydispersity and with designed terminal functionalities. It is also possible to make block and graft copolymers, star-like, comb-like and cyclic macromolecules. This level of macromolecular control is possible using living polymerization approach[1,2]. It is also possible to control arrangements of substituents in the chain i.e., control chemoselectivity, regioselectivity and stereoselectivity. Control of the microstructure and tacticity usually requires heterogeneous catalysis when control of chain dimensions and polydispersities is not possible. Living polymerization has been successfully used for the anionic polymerization of non polar and polar monomers[1,3,4], cationic polymerization of heterocyclics[5] and alkenes[6] and for the metathesis polymerization of cycloalkenes[7]. Unfortunately not all monomers can be polymerized via truly living methods. Sometimes molecular weights have to be limited to suppress (or hide) transfer and termination reactions[8].

A new class of inorganic and organometallic polymers gets increasing attention and importance[9,10]. Some of these polymers behave as low temperature elastomers, some have flame resistance, some are bioinert, some have extremely useful surface properties, others show special electronic and optical effects. However, at present, most inorganic and organometallic polymers are available as ill-defined materials with extremely high polydispersities (often with polymodal molecular weight distribution), non-controlled degrees of polymerization and unknown end groups. Some applications, particularly those in biomedical and optoelectronic fields, require well-defined polymers. In this paper we will focus on polysilylenes (polysilanes) and polyphosphazenes, two important classes of inorganic and organometallic polymers studied in our laboratories. Possibilities of the improvement of the structural control in these polymers will be discussed.

POLYSILYLENES

Polysilylenes are polymers with a linear Si-Si catenation in the main chain and with two organic substituents at each silicon atom. Most polysilylenes contain alkyl and aryl substituents. They have unusual physical and chemical properties and are of a potential commercial importance[11,12,13]. Symmetrically substituted polymers usually do not melt to isotropic state but transform from crystalline state to a columnar mesophase[14]. Electrons in the main chain are delocalized leading to materials with extremely interesting electronic properties: semiconductors, photoconductors, and nonlinear optical materials [12,15,16,17,18]. Applications in microlithography are based on the photosensitivity and photobleaching of polysilylene chains[12,15]. Electronic and optonic materials based on polysilylenes should have well defined structures because some properties depend on molecular weights, chain substitution and chain conformation. Therefore, we are developing new synthetic methods which will allow better control of the structure of polysilylenes.

The most common synthesis of polysilylenes is based on the reductive coupling of disubstituted dichlorosilanes with alkali metals[19,20]. Usually polymodal products are formed which disables some applications[12,13] The dehydrogenative coupling in the presence of transition metals provides materials with too low molecular weight[21,22]. There are two new routes to polysilylenes based on the anionic polymerization. First one employs "masked disilenes"[23] and the second one strained cyclotetrasilanes[24]. These techniques provide additional control of the microstructure. In this paper some of our recent activities in the synthesis and characterization of polysilylenes will be discussed. These include mechanistic studies of the sonochemical reductive coupling process, ring opening polymerization, and reactions on polysilylenes, i.e. modification and grafting, as well as formation of some random copolysilylenes.

Reductive Coupling Process

Reductive coupling of disubstituted dichlorosilanes with alkali metals is a chain (not a step) polymerization. Polymers with very high molecular weights are formed at low conversions and independently of the [Mt]/[Si-Cl] ratio. Several intermediates such as silylene, radicals, and anions have been proposed as potential chain carriers. In the initial slow stage, radicals may play an important role. However, oligosilanes will further polymerize via anionic intermediates. Strong solvent, additive, metal, and substituents effects suggest propagation by the reaction between ....-SiSi-Mt intermediates and a monomer, followed by a fast reduction of ....-SiSi-Cl to ...-SiSi-Mt. The exact nature of the Si-Mt bond is still obscure and, under some conditions, it might have a partial covalent character. The reasons of the bimodality of the obtained polymers is not yet clear. Low molecular weight fraction may be formed by macrocyclization but some end groups were observed; in addition, a distribution of this product does not obey statistics tpical for macrocyclization. It is possible that relatively long chains, at a certain critical molecular weight, split into two fractions. One of them "sticks" to the surface of alkali metal and continues to grow to high molecular weight and the other one departs to solution and is not able to find its way back to the surface. It is also possible that some side reactions may at this stage terminate chain reactivity. It seems that at lower reaction temperature, proportion of the side reaction decreases and exclusively high molecular weight materials could be formed[25,26].

In order to facilitate low temperature synthesis we activated surface of sodium with ultrasound[27]. Under sonochemical conditions (ambient temperature) polymers with high molecular weights (M_n from 50,000 to 100,000) and low polydispersity (M_w/M_n from 1.2 to 1.5) were formed. There are two phenomena responsible for the more selective polymerization. First, lower polymerization temperature and continuous removal of the sodium chloride from the sodium surface suppresses formation of the low molecular weight polymer (M_n from 2,000 to 10,000). Second, ultrasound mechanically degrades polysilylenes with molecular weights above 50,000. This limit is probably set by the chain entanglement and Si-Si bond stability. Polysilylenes of sufficiently high molecular weight prepared in separate experiments could also be selectively degraded. It seems that degradation in toluene in the presence of alkali metals is slightly accelerated, but no low molecular weight cyclooligosilanes are formed. On the other hand, in THF and diglyme (or in toluene in the presence of cryptands and potassium) polymer is completely degraded to cyclohexasilanes and cyclopentasilanes[28]. The anionic intermediates have been observed spectroscopically in this degradation. Not only degradation but also polymerization is sensitive to solvent and metal nature. In toluene, using sodium as a reducing agent, monomers with aryl groups polymerize much faster than dialkylsubstituted dichlorosilanes[27]. The latters require elevated temperatures (above 80 °C), although they react readily with Na/K and K. However, phenylmethyldichlorosilane does not react with potassium within 2 hours under similar conditions. Apparently, no oligosilanes capable of anionic polymerization can be formed, and intermediate radicals react with toluene[29].

Copolymerization of various dialkylsubstituted dichlorosilanes by a reductive coupling process not always leads to statistical copolymers. The copolymerization is controlled by the reactivity of monomers and the electron affinity of a polysilylene. Thus, dichlorosilanes with aryl groups are much more reactive than those with alkyl groups. It seems also that dimethyldichlorosilane has a tendency to form blocky structure when copolymerized with other dialkyldichlorosilanes. On the other hand, we found that copolymerization of di(n-hexyl)dichlorosilane with di(n-butyl)dichlorosilane and di(n-propyl)dichlorosilane leads to statistical copolymers. The copolymer composition corresponds to the monomer feed and the distribution of various triads, pentads, and heptads roughly corresponds to Bernoullian statistics.

Ring-Opening Polymerization

The majority of known cyclooligosilanes are thermodynamically stable and cannot be converted to linear polymers. The ring size depends on the size of substituents. Six membered ring is preferred for silicon atoms with two methyl groups, five membered for majority of simple alkyl and aryl groups. However, bulky tert-butyl groups lead to cyclotetrasilanes and even larger mesityl groups to cyclotrisilanes. Some potentially strained rings such as octaphenylcyclotetrasilane can be prepared in high yield due to low solubility, high melting point and moderate size of substituents. The attempts to polymerize this ring led only to isomerization to more stable decaphenylcyclopentasilane. Thus, the ring is potentially strained but the monomer could not be polymerized. On the other hand, the reductive coupling of methylphenyldichlorosilane leads to a polymer and a mixture of five- and six-membered rings, no four-membered ring is formed. Thus, it would be very interesting to prepare cyclotetrasilane with methyl and phenyl groups. Reactivity will be higher than for the perphenylated ring and solubility better for both a monomer and for a polymer[30]. We have discovered rapid and clean displacement of phenyl groups in oligosilanes with trifluoromethanesulfonic acid[31]. Reaction of octaphenylcyclotetrasilanes with four equivalents of the acid leads to 1,2,3,4-tetra(trifluoromethanesulfonyloxy)-1,2,3,4-tetraphenylcyclotetrasilane. Subsequent reaction with either methylmagnesium iodide or methyl lithium yields four stereo isomers of 1,2,3,4-tetraphenyl-1,2,3,4-tetramethylcyclotetrasilane.

A Si-Si bond can be cleaved by strong electrophiles and nucleophiles. Reaction with silyl anions leads to ring-opening and to the regeneration of silyl anions[30]. This is the propagation step. Silyl anions may also attack the Si-Si bonds in the polysilylene chain and form macrocycles and strainless cyclooligosilanes (degradation). Rates of polymerization and degradation depend on solvent, temperature, and alkali metals. With 1 mol% of silyl potassium or butyl lithium initiator, only cyclooligosilanes have been found after less than 2 minutes at room temperature in pure THF. In mixtures of 60 % THF with benzene polymerization is completed within less than 2 minutes, but degradation starts after 1 hour. In benzene, with less than 3% THF, polymerization is completed after more than 1 hour. Similar rate is observed in pure benzene but with a catalytic amount of crown ether (crown-4 for lithium) or cryptand (cryptand [2.1.1] for lithium). No degradation was found under this conditions within a few hours. Polymers with molecular weights from 10,000 to 100,000 have been prepared via the anionic ring-opening polymerization of cyclotetrasilanes. This technique provides a pathway to various functional polymers and block copolymers.

Polysilylenes with Triflate Groups

The dearylation with triflic acid can be also applied to polymers. We used this technique to partially displace phenyl groups from poly(methylphenylsilylene). The rate of the dearylation is strongly influenced by the presence of an electron withdrawing group at the neighboring Si atoms. Model studies on dearylation of α,ω-diphenylpermethyloligosilanes with triflic acid indicate that the displacement of the first phenyl group is always faster than that of the second, even for pentasilanes[31]. Thus, at relatively low degree of substitution, triflate groups are separated by non-modified blocks.

The dearylation process applied to polysilylenes containing phenyl substituents provides polymers with strong electrophilic silyl triflate moieties. Silyl triflates belong to the strongest known silylating reagents. They can react with such nucleophiles as alcohols, amines, carbanions, organometallics, etc. This opens a new synthetic avenue towards various functional polysilylenes[32,33]. The reactivity of silyl triflates is so high that they can initiate cationic polymerization of some alkenes and heterocyclics to form graft copolymers.

We investigated possibility of initiation with silyl triflates for various alkenes and heterocyclics. Initiation is usually slow and inefficient. For example, polymerization of styrene, can not be initiated at all by trimethylsilyl triflate[34]. Rate constant of initiation of oxazoline and THF is more than 1,000 slower than rate of propagation. However, we also found that use of promoters such as ketones and oxiranes can dramatically increase rate constants of initiation and lead to the synthesis of well-defined polymers[35]. This technique can also be applied to graft copolymers.

POLYPHOSPHAZENES

Polyphosphazenes are interesting inorganic polymers which find applications as advanced materials with low temperature flexibility, superb solvent and oil resistance, flame resistance, toughness, and vibration damping and also as potential biomaterials[9,36].

Polyphosphazenes can be formed by various methods. The first one is based on the ring-opening polymerization of hexachlorocyclotriphosphazene at approximately 250 °C and the subsequent displacement of chlorine atoms by alkoxy and aryloxy substituents[9]. Unfortunately, this method leads to polymers with high polydispersities. Application of Lewis and protonic acids as catalysts reduces polydispersities and also reduces molecular weights.[37,38]

The second route employs the high temperature (200 °C) condensation of N-silylphosphoranimines and provides polymers with alkyl and aryl substituents directly bound to phosphorus[39]. Polyphosphazenes can also be formed by high temperature condensation of P-trichloro-N-dichlorophosphoryl monophosphazene[40] and by phosphine azide intermediates[41]. None of these methods, however, allows control of molecular weights or leads to well-defined materials.

We recently demonstrated that polymerization of N-trimethylsilyl-tris(trifluoroethoxy)phosphoranimine initiated by salts containing fluoride anions at a temperature of 100 °C leads nearly quantitatively to a linear polyphosphazene with molecular weight in the range of M_n=20,000 to 100,000 and relatively narrow polydispersities ($M_w/M_n < 1.5$)[42]. We focus on the control of molecular weights and structure of the end groups in this polymer. Some new initiators and new monomers polymerized by the anionic mechanism will be discussed.

The second approach is based on polymerization via phosphine azides as intermediate products. This polymerization, in contrast to previous reports, can be controlled and lead to the formation of new polyphosphazenes which can not be obtained by "classic" methods[43].

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